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14. ABSTRACT

This report results from a contract tasking RWTH Aachen as follows: A new class of machinable ceramic materials had recently received attention due a unique combination of hardness, toughness, machineability, and oxidation stability. These materials are called MAX phases, where M designates a transition metal, A is mostly a IIIA or IVA element of periodic table, and X stands for C or/and N. MAX phases have a unique nanolaminated atom arrangement, which leads to a low shear modulus - a property critical for low friction materials. However, MAX phases for tribology have not yet been explored systematically. Most research has been done on the machinable Ti3SiC2 system. However, the list of theoretically possible MAX phases is extensive. Practically, it is resource intensive to synthesize every thinkable MAX phase searching for a material exhibiting advantageous tribological properties. A superior strategy is to calculate bonding, structure, and properties of possible MAX phase compounds and then selectively dedicate a synthesis effort to the phase with the best combination of properties. This project is based on state of the art (1998 Nobel Prize in chemistry) density functional theory calculation algorithms to build up models of MAX phases and provide predictions of their phase stability and expected properties. It is envisioned to systematically explore nanolaminated phases with the M2AlC formula to address the influence of the M elements (Y, Zr, Nb, Mo, La, Hf, Ta, W) on bonding strength, electronic structure, and shear modulus. Our aim is to contribute towards the development of novel tribological materials. We propose to study the relationship between the valence electron configuration of M = Y, Zr, Nb, Mo, La, Hf, Ta, and W in M2AlC and the shear modulus of this fascinating new class of nanolaminated materials.

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FINAL REPORT (ITEM 0005)

Ab-initio Calculations of Structure and Properties of Nanolaminated MAX Phases

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Our aim is to contribute towards the development of novel tribological materials. We study the relationship between the valence electron configuration of M in M_2AlC and the shear modulus of this fascinating new class of nanolaminated materials.
Our specific research directions are:

Goal 1: To find the minimum shear modulus in M_2AlC with M = Y, Zr, Nb, Mo. This has been carried out within Part A.

Goal 2: To find the minimum shear modulus in M_2AlC with M = La, Hf, Ta, W. This has been carried out within Part B.

Figure 1 shows a comparison between the C_{44} values of M_2AlC (M = Y, La, Zr, Hf, Nb, Ta, Mo, W) and the C_{44} data of the corresponding MC. It is interesting to note that the C_{44} values of M_2AlC are close to those for MC, except for M_2AlC phases containing groups VB and VIB transition metals. Hence, M_2AlC may be classified into two groups according to valence electron concentration of the transition metal M. One group comprises groups VB and VIB transition metals, where the C_{44} values are constant at about 170 GPa and independent of the corresponding MC. The other group includes transition metals of groups IIIB and IVB, where the C_{44} is a linear function of the corresponding MC. The valence electron concentration induced changes in shear behavior observed here can be compared to previously published valence electron concentration induced changes in compression behavior[1,2]. It is evident that both classification proposals exhibit identical critical valence electron concentration values for the group boundary. Furthermore, it is worth noting that the C_{44} data of Y_2AlC and La_2AlC are comparable to those of Au and Ag[3], which are common solid lubricants[4]. Hence, it is envisioned that these ternary carbides may benefit a number of applications, one of which is a low shear strength solids to operate at elevated temperatures without degradation by oxidation and wear.

The shear stress – shear strain relationship for M_2AlC with M being a 4d transition metal is shown in Fig. 2. It is obvious that the previously discussed two-group behavior is conserved. Y_2AlC and Zr_2AlC can be described as weakly coupled M_2AC phases, while Nb_2AlC and Mo_2AlC are strongly coupled. Furthermore, there is a peak (yield point) in the stress – strain curves of Mo_2AlC and Nb_2AlC at 0.30, while Zr_2AlC and Y_2AlC exhibit the corresponding peaks at 0.28 and 0.25, respectively.

[1] Z. Sun, D. Music, R. Ahuja, S. Li, and J. M. Schneider, Phys. Rev. B **70**, 092102 (2004)
[2] D. Music, Z. Sun, and J. M. Schneider, Solid State Commun. **133**, 381 (2005)
[3] C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, New York, 1996) p. 91
[4] O. O. Ajayi, A. Erdemir, G. R. Fenske, R. A. Erck, J. H. Hsieh, and F. A. Nichols, Tribology Trans. **37**, 656 (1994)

Thus, Mo_2AlC and Nb_2AlC withstand larger shear strains than Zr_2AlC and Y_2AlC. This is reflected in the ideal shear strength of these compounds decreasing from 54.7 to 7.5 GPa, by 83.3%, as Mo is replaced with Y in M_2AlC. We have shown for Nb_2AlC that it exhibits basal slip and there is no evidence of phase transformation under shearing[1]. This is consistent with all shear stress – shear strain relationships shown in Fig. 2. The classification proposal for shearing put forward here may be corroborated by these stress – strain relationships.

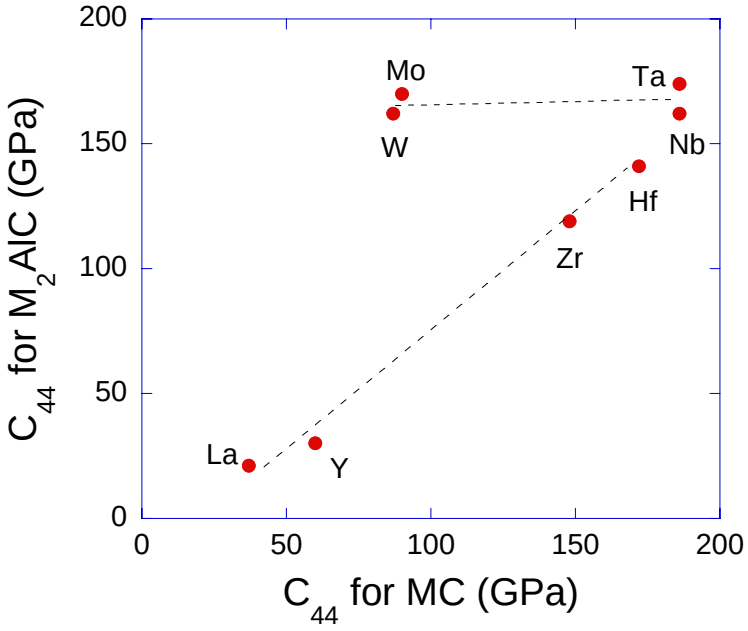

FIG. 1 Elastic constant C_{44} of ternary M_2AlC phases (M = Y, La, Zr, Hf, Nb, Ta, Mo, W) as a function of C_{44} of the corresponding binary carbides.

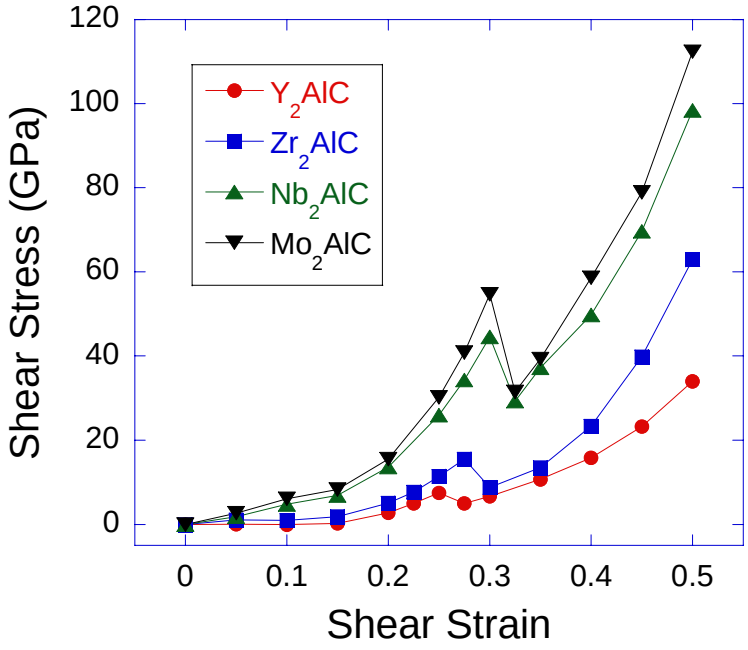

FIG. 2 The stress-strain curves for the shear deformation in M_2AlC, where M is Y, Zr, Nb, and Mo.

[1] D. Music, Z. Sun, A. A. Voevodin, and J. M. Schneider, submitted for publication (2005)

This behavior may be explained by the analysis of the electronic structure. In Fig. 3, electron density distributions in the $(11\bar{2}0)$ plane for M_2AlC, where M is Y, Zr, Nb, and Mo, are shown. Analyzing the M-C bonding, it can be concluded that the bonding is characterized by covalent and ionic contributions. There is metallic bonding between MC and Al layers as well as weak covalent contribution in c-direction as a function of valence electron of M. Hence, Y_2AlC and Zr_2AlC may be characterized as weakly coupled nanolaminates, while Nb_2AlC and Mo_2AlC may be characterized as strongly coupled nanolaminates. This may be an explanation for the shearing behavior: weakly coupled nanolaminates give rise to low C_{44}, while strongly coupled nanolaminates give rise to large C_{44}, as discussed above.

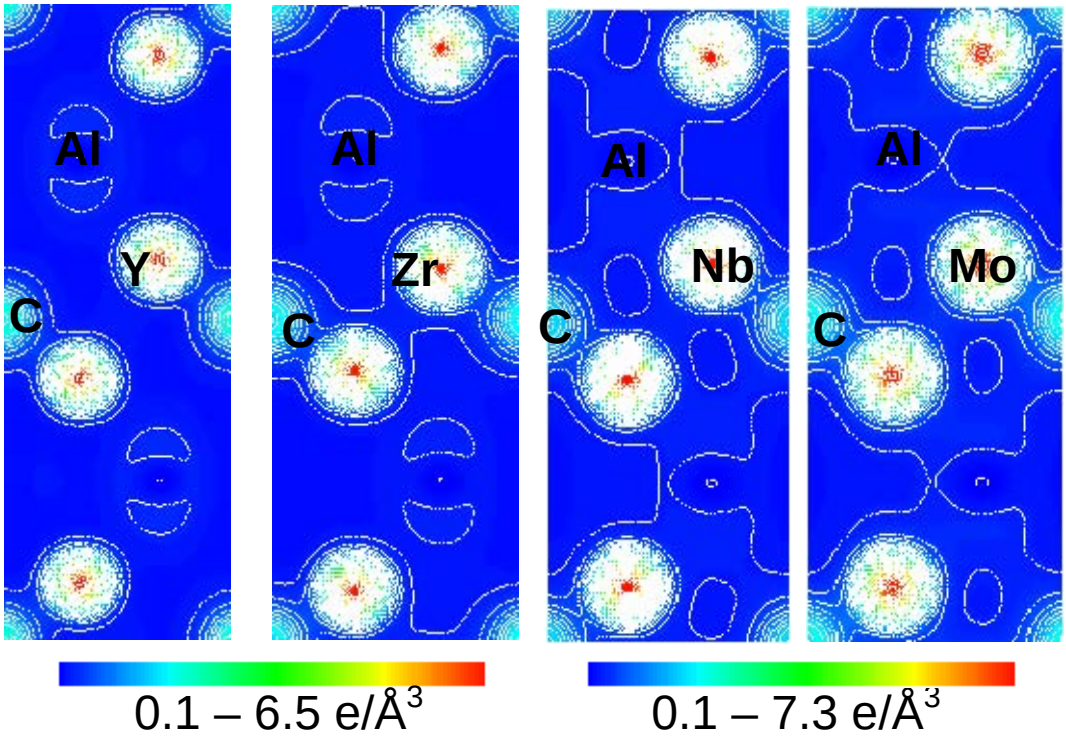

FIG. 3 Electron density distributions in the $(11\bar{2}0)$ plane for M_2AlC, where M is Y, Zr, Nb, and Mo.

In summary, we have carried out systematic research on the relationship between the valence electron configuration of M (Y, Zr, Nb, Mo, La, Hf, Ta, W) in M_2AlC and the shear modulus of this fascinating new class of nanolaminated materials. It can be learned that M_2AlC phases with M from group IIIB exhibit the lowest shear modulus. This can be understood based on weak coupling of these nanolaminates in the c-direction. These findings may be important for the development of low friction ceramic based materials, which are capable of a broad temperature range operations. These materials can be then incorporated into advanced nanostructures for broad temperature lubrication in ambient and space environments, which are currently being developed for aerospace engineering. Furthermore, since such materials contain intrinsically nanolayered arrangements of metal/covalent-ionic bond interfaces, their friction response can be influenced through substitution of M and A elements to tune tribo-chemical activated reactions and processes.